Preparation and investigation of the screen-printed cobalt oxide (Co₃O₄) nanostructured thick film with annealing temperature

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ABSTRACT In this study, spinel type cobalt oxide (Co₃O₄) thick films are deposited on glass substrate by screen printing technique. All characterization was carried out for unannealed, annealed at 250 – 400 °C. The X-ray Diffraction (XRD) analysis indicates that prepared films have polycrystalline nature with cubic structure having preferential orientation through (311) plane. Crystallite size is found to be 18.52 nm. The lattice parameter found to be 8.036 – 8.138 Å approaches to standard value ($a = 8.08$ Å). Scanning Electron Microscopy (SEM) analysis of prepared films shows agglomeration of nanoparticles, occurrence of spherical-shaped grain aggregations. Spherical grain size increases from 47.66 to 77.33 nm with increase in annealing temperatures. A relation between structural and morphological properties is noted. The Energy Dispersive Analysis by X-Ray (EDAX) shows that all compositions have desired stoichiometric ratios. Besides electrical measurements, film D.C. resistance, resistivity was measured. It allows us to conclude that assured material has semiconducting nature. Specific surface area, Temperature Coefficient of Resistance (TCR), activation energy decreases with increase in annealing temperature were calculated. It was shown that structural, morphological and electrical properties of Co₃O₄ films were improved by increasing annealing temperature.

1. Introduction

Recently, transition metal oxides (TMOs) attracted great attention as an important and promising materials which have remarkable electronic, optical, magnetic, and catalytic properties. Cobalt oxides nanoparticles exhibit interesting properties and applications when compared with bulk. It is a p-type cubic spinel structure semiconducting material with two direct and indirect optical bandgaps (1.44 – 2.06) eV and (1.26 – 1.38) eV, respectively. Bulk cobalt oxide crystals appear in two stable crystallographic structures, the rock salt-type CoO and the normal-spinel-type Co₃O₄. One can mention applications in different areas such as smart windows, negative electrodes in Li-ion batteries and mirrors with variable reflectance. Basically, Co₃O₄ is an electrochromic material and would be classified into two categories: cathodic like molybdenum oxide, tungsten oxide etc, and anodic coloured materials like ruthenium oxide, cobalt oxide, nickel oxide, etc. [1].

Among transition metal oxides, great attention has been focussed on spinel type tricobalt tetra oxide is versatile metal oxides because of its two characteristics, namely, variable valence state and existence of oxygen vacancy defects. It exists in different forms such as CoO2, Co₂O₃, CoO (OH), Co₃O₄ and CoO. In these, Co₃O₄ acquires the normal spinel structure: magnetic Co²⁺ (3d⁷) cations are placed in tetrahedral sites and nonmagnetic Co³⁺ (3d⁶) cations occupied octahedral ones. In bulk crystalline, Co₃O₄ renders antiferromagnetic material while in nanostructures, it shows weak ferromagnetism with an energy band-gap of 1.4 – 1.8 eV [2]. On the other hand, semiconductor nanoparticles have attracted a great study of interest owing to their enhanced and exclusive properties when the surface to volume ratio increases. Due to its good chemical stability and high specific surface area, therefore it is used in field of gas sensors for detection purpose [3]. In most of the research work the Co₃O₄ has been selected for investigation, because of its chemical stability, desired electrochemical property and high annealing temperature. Usually, SMO gas sensors worked at high temperature ($\geq$ 150 °C), and their response strongly depends on temperature. Also, kinetic reactions between semiconductors and gases are temperature dependent [4]. This Co₃O₄ phase can be easily obtained in air atmosphere. Cobalt

oxide thin and thick films are prepared by different methods such as atomic layer deposition, sol-gel technique, chemical vapour deposition, RF magnetron sputtering, chemical bath deposition, screen printing technique, spray pyrolysis and nebulizer spray pyrolysis.

Among these techniques, screen printing technique has many advantages such as low cost, easy to handle, convenient for large area deposition, uniform film deposition and less deposition time. This technique has been employed by many researchers to fabricate thick films of tin oxide, cerium oxide, zinc oxide and indium oxide. [5, 6]. After preparation, films are ready for characterization by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, electrical conductivity measurement etc. During synthesis of Co_3O_4 nanostructures, many efforts have been taken by researchers with different morphologies such as hollow spheres, nano porous, nanospheres, nanotubes cubic single crystals, nano particles, nano rods, nano plates, nano wires, and nano cubes structures [7]. Improvement in the electrical conductivity, transmission stability and practical feasibility possible by different processes like doping, annealing and aging. Structural and morphological properties were improved by heat treatment. After annealing crystallinity, grain size of the film increased due to diminishing of oxygen vacancies and film surface area became smooth, reduces crystal defects [8]. Therefore, We say that annealing treatment can activate oxygen vacancies and also enhanced crystal quality of the nanostructure.

Film annealing up to 200 °C results crystal having low-quality. Based on earlier studies it is interesting to study about Co_3O_4, and its associated various properties of prepared screen-printed Co_3O_4 thick films and the effect of annealing temperature on it are important now a days.

Screen-printing technology has been demonstrated which is suitable for mass-production of thermoelectric modules with advantages [9]. Structural characterization, surface morphology and particle size of the samples were determined from XRD technique, scanning electron microscopy (SEM) instrument while the stoichiometric characteristic was proved from energy dispersive X-ray analysis [10].

In the present study, we have reported preparation of screen printed Co_3O_4 thick films and investigates the effect of annealing temperature on structural, morphological and electrical characterization elaborated by a simplified screen-printing technique.

2. Materials method and measurements

The commercially available AR grade with 99.99 % purity cobalt oxide nano powder was used for preparation of thick films. Other than this, chemicals required for preparation of thick films are acetone, ethyl cellulose, B.C.A., etc purchased from Scientific Lab, Nashik. To verify structural properties and purity of samples, the X-ray diffraction (XRD) technique is used. The X-ray diffraction patterns of all the prepared samples are recorded for analysis purpose. They were plotted using Bruker D8 advance diffractometer, Germany with CuKα ($\lambda = 1.54$ angstrom) radiations operated at 40 KV and 40 mA in the scanning range of (2θ) between 20 ° and 80 °. To observe chemical compositions and surface morphology, scanning electron microscopy named as SEM-JEOL JSM-6360A with OXFORD EDS attachment is used. For electrical characterization, simple half bridge method was used.

2.1. Preparation of thick films of cobalt oxide nanoparticles

The cobalt oxide based thick film sensor was constructed by standard screen-printing technique. The powder nanoparticle of Co_3O_4 converted into paste form was used to prepare thick films by maintaining the inorganic (Co_3O_4) to organic binder ratio as 70:30. The organic binder contains of 8 % ethyl cellulose (EC) which is in a powder form and 92 % butyl carbitol acetate (BCA) present in a liquid form. All these stoichiometric amounts of Co_3O_4 and binders then mixed mechanochemically into mortar and pestle and crushed continuously for nearly 40 minutes. A solution of BCA which add on drop wise in order to get correct viscosity for screen printing. Prepared gel like paste can employed over glass substrate with dimensions 1.5×2 cm. After completion of thick film coating, these films were air dried firstly for 30 minutes followed by IR drying for 30 minutes. Finally, the prepared binary oxide Co_3O_4 film sensor was kept in muffle furnace for calcinations process at various temperatures 250, 300, 350, 400 °C nearly 2 hours. After annealing films became black in colour and found to be uniform, pinholes free and strongly adherent to the glass substrates. Such annealed films are now ready for characterization.

2.2. Measurement of the film thickness

The thickness of the prepared films calculated by the using gravimetric (weight-difference) method assuming the samples were approximately uniform as compares to bulk form. Thickness measurement equation is given by

$$t = \Delta w / A \cdot \rho, \tag{1}$$

where Δw – actual weight of the prepared film, $\rho = 6.11$ gm/cm^3 – density of Co_3O_4, A is the area of the film (length $\times$ breadth).

Screen-printed thickness observed range varies from 33 to 38 μm.

2.3. Characterisation of screen printed Co_3O_4 thick film sensor

The physical (structural), chemical properties and experimental performance of cobalt oxide NPs intensively depends on size, shape geometry, morphology etc. To characterise the prepared samples mainly X-ray diffraction technique (structural analysis), scanning electron microscopy with EDS (morphological and elemental analysis) and half bridge method (electrical analysis) were used. The success of the synthesised nanoparticles was easily confirmed by characterisation techniques.

3. Results and discussion

3.1. Structural characterisation: XRD analysis (Crystal structure determination)

The structural properties of thick film is the key to recognize its quality, the crystallinity and phases of transition metal oxides nanoparticles and composite nanoparticles were analysed by X-ray diffraction technique [11]. For recognition of the crystalline phase, JCPDS (Joint Committee on Powder Diffraction Standards) data and using Debye–Scherrer equation the crystallite size was calculated.

Figure 1(a–e) shows the XRD patterns of Co_3O_4 thick films as deposited at room temperature (unannealed) and annealed at different temperatures namely 250, 300, 350, 400 °C. It indicates the purity of the product. From XRD study, diffraction peaks are located at 2θ of 31.0730, 36.7490, 38.470, 43.130, 44.710, 55.520, 59.250 and 65.160 indicating their polycrystalline nature corresponding to (220), (311), (222), (400), (422), (511), and (440) crystal planes, respectively. This demonstrated the formation of Co_3O_4 with cubic crystal structure as per [JCPDS card no. 42-1467]. The peak intensity is strong, indicating high crystalline structure of the products [12]. The average crystallite size of the Co_3O_4 thick films is estimated from the X-ray diffraction patterns using the Debye–Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta}, \tag{2}$$

where D is the crystallite size, β is the Full Width at Half Maxima (FWHM), λ is the wavelength of X-ray used and θ is the diffraction angle.
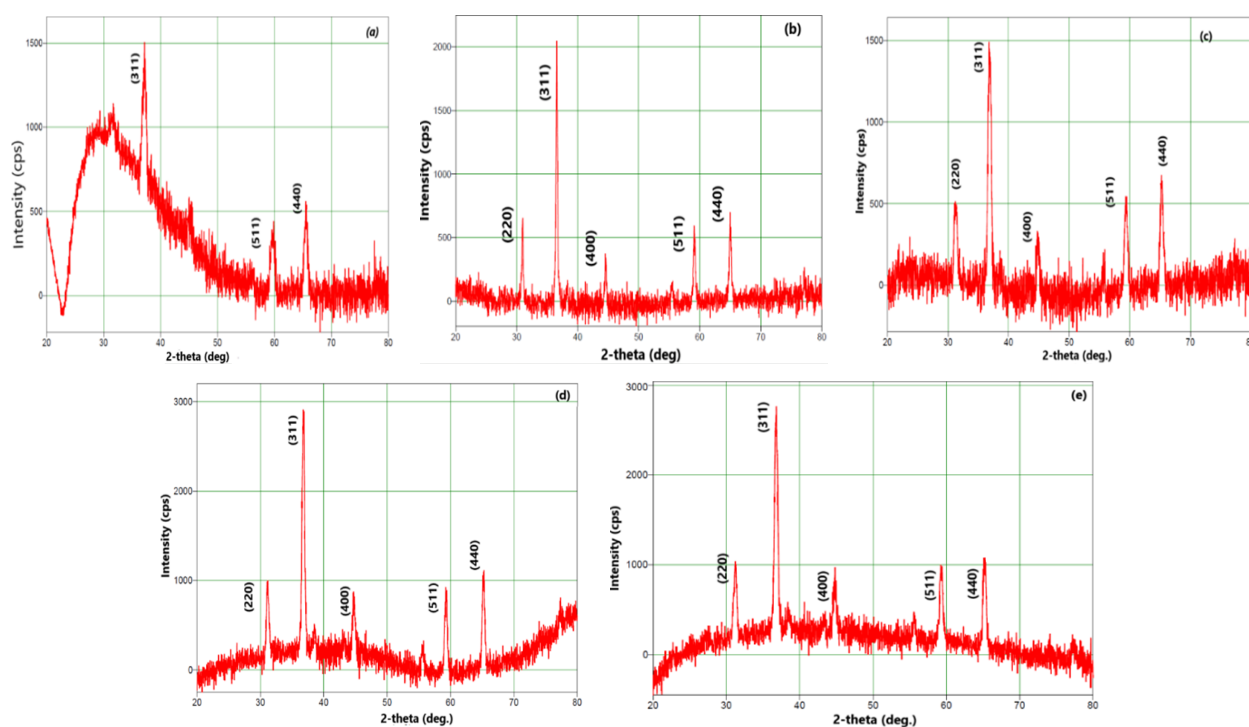

FIG. 1. XRD patterns of Co_3O_4 thick films as deposited (unannealed) (a), annealed at 250 °C (b), 300 °C (c), 350 °C (d), 400 °C (e) respectively

The crystallite size of Co_3O_4 calculated from the strongest peak, located at (311) plane at $2\theta \approx 37$ °, are estimated as 18.52 nm. The average crystallite size for pure cobalt oxide was found to be 18.20 nm [13, 14] and its distribution range lies from 18.52 to 36.38 nm depending on annealing temperature.

The obtained value of d_{hkl} (interplanar distances) values and the standard values confirm that the deposited and annealed films are nano crystallized in the spinel type cubic structure of Co_3O_4. The lattice parameter a of the unit cell is calculated from the peak positions using the formula of cubic system Formula. This value is found to be in the range

8.036 –8.138 Å, which is close to standard value ($a = 8.08$ Å) given by JCPDS 42-1467. When the annealing temperature increases, the intensity of the peak corresponding to the (311) plane is found to decrease due to the thermal strain. Sharp diffraction peaks are observed at 350 °C annealed temperature [15].

From XRD data, the crystalline parameters like lattice constant (a), crystallite size (D), dislocation density (δ), and micro strain (ε) were determined. The dislocation density is the length of dislocation lines per unit volume of the crystal. Greater D and smaller δ values mean better crystallization of the films. The dislocation density and lattice strain were calculated from the diffraction pattern to obtain more information about structural properties. The observed changes of strain take places due to point defects and crystallite size. The lattice strain is calculated using Stokes–Wilson equation. To know more on the number of defects in the film, the dislocation density (δ) is calculated by using relation mentioned in Table 1. The induced strain causes reduction in crystallite size and increase in peak broadening. The average micro strain screen printed Co$_3$O$_4$ thin film sensor is 0.27 %. Micro strain decreases from 0.00611 to 0.0009 due to good crystallinity.

TABLE 1. Shows dislocation density and micro strain for different annealing temperatures

Annealing temperature (°C)	Dislocation density $\delta = 1/D^2$ (lines/m^2) 10^{15}	Micro strain $\varepsilon = \beta \cos \theta / 4$, 10^{-3}
Unannealed	13.18	6.11
250	0.75	0.952
300	5.10	2.475
350	2.92	1.870
400	3.695	2.1

The XRD spectrum is in full agreement with the standard spectrum of cubic crystalline Co$_3$O$_4$. JCPDS card no: (42–1467). The diffraction peaks revealed to the cubic nature of nanocrystalline Co$_3$O$_4$.

3.2. Morphological characterization

3.2.1. SEM with EDS analysis (surface morphology). The Scanning Electron Microscopy (SEM-JEOL JSM 6360 Model) images of prepared nanomaterial Co$_3$O$_4$ thick film are displayed in Fig. 2. These 2D images with high magnification show surface texture, color and porosity Co$_3$O$_4$ nanoparticles and indicate the formation of particles with different shapes and sizes. This porosity may be due to the evaporation of organic binder during the growing process and annealing treatment [16]. The surface characteristics of the prepared films investigated by scanning electron microscopy that shows heterogeneous, porous nanoparticles with varying dimensions. The observed particles are highly agglomerated and they are essentially cluster of nanoparticles. The surface morphology of screen printed Co$_3$O$_4$ thick films shows that small sphere-shape particles are distributed. Some of them have heterogeneous surface, microspores and mesopores as seen from its surface micrographs [8]. It's greyish black in color, various sized nanoparticles image can be seen from SEM images as shown.
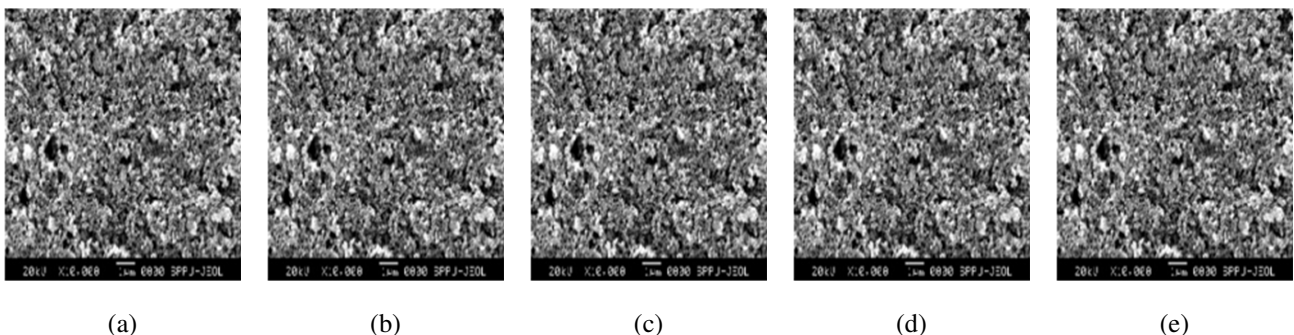

(a)   (b)   (c)   (d)   (e)

FIG. 2. SEM micrographs as deposited (unannealed) (a), annealed at 250 °C (b), 300 °C (c), 350 °C (d), 400 °C (e) Co$_3$O$_4$ thick films respectively

Micrographs shows surface morphology of Co$_3$O$_4$ thick films deposited on glass substrate annealed at unannealed, 250, 300, 350, 400 °C with higher resolution. It is observed that films show polycrystalline nature with no. of voids (pores) distributed on the surface of film. The particle size was obtained as the length of the segment joining the two ends of the particle and passing through its mass centre and the average particle size was measured using image software, increases

from 73 to 145 nm with increase in annealing temperatures. It is maximum when film is unannealed. The average particle size is 116.702 nm. Spherical grain size increases with respect to annealing temperature and its change from 47.66 to 77.33 nm and it has maximum when thick film is unannealed. Surface area decreases from 20.60 to 12.698 m^2/gm with increase in annealing temperature and is a minimum for unannealed film as shown in Table 2. Surfaces of Co$_3$O$_4$ thick films are cubical, spherical grains, so such a film can adsorb more atmospheric oxygen due to more exposed surface area of the film. Highly porous film shows high sensitivity.

TABLE 2. Mean particle size, grain diameter and surface area at various annealing temperatures

Annealing temperature (°C)	Mean particle size (nm)	Spherical grain diameter d (nm)	Specific surface area $S_w = \dfrac{6}{\rho d}$ (m^2/gm)
Unannealed	127.2	83.5	11.76
250	73.11	47.66	20.60
300	108.2	66.66	14.73
350	130	73.66	13.33
400	145	77.33	12.698

3.2.2. EDS Analysis. The elemental quantitative composition of grown Co$_3$O$_4$ nanoparticles was determined using the spectra obtained by energy dispersive analysis of X-rays (EDAX). The weight percentage and atomic percentage of cobalt oxide nanoparticles are shown in Table 3. This declares proof that synthesized nanoparticles are non-stoichiometric. In cobalt oxide this nonstoichiometric is accompanied by change in colour with the stoichiometrically correct cobalt oxide being grey and non-stoichiometric being black. Fig. 3 shows elemental composition annealed Co$_3$O$_4$ thick film sensors.

TABLE 3. Atomic % elemental composition of Pure Co$_3$O$_4$ thick films as measured by EDS

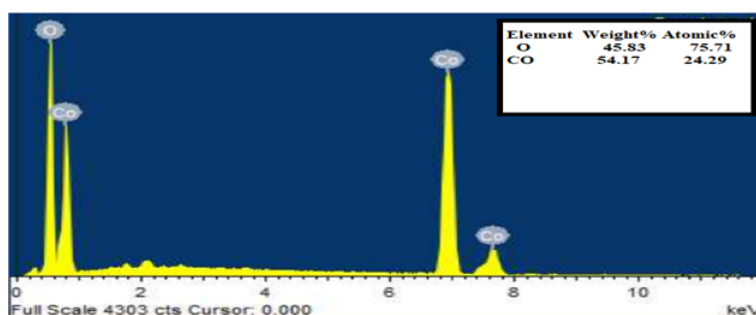| Sample annealed temperature	Elements				Co/O Ratio
	Co		O		
	At. wt. %	*At. Mass %*	*At. wt. %*	*At. Mass %*	
Unannealed	53.90	24.09	46.10	75.91	1.17
250 °C	52.21	22.88	47.79	77.12	1.09
300 °C	53.76	23.99	46.24	76.01	1.16
350 °C	54.43	24.24	45.57	75.71	1.19
400 °C	54.17	24.29	45.83	75.51	1.18

FIG. 3. EDAX results of Co$_3$O$_4$ nanoparticle

3.2.3. EDAX results of Co₃O₄ nanoparticles. The weight percentage of cobalt is increased with annealing temperature and mass percentage of oxygen decreases with increasing annealing temperature due to the release of excess oxygen. decreases which indicates the oxygen adequate nature of the films [17].

Table 3 shows quantitative elemental analysis of Cobalt oxide thick films. In figure, the major peaks of Co and O elements are observed. The observed compositional data from the EDX analysis responds positively with theoretically calculated values, representing a good elemental compositional homogeneity across the cobalt oxide nanoparticles. The EDX spectrum shows sharp peaks between 6.6 and 7.8 KeV for Co and between 0.4 and 0.6 KeV for O corresponding to crystalline Co₃O₄ NPs. The EDAX results obtained for spinel type cobalt oxide thick are in good agreement with reported output. The straightforward stoichiometry of Co:O in case of Spinel type cobalt oxide was 3:4; is considerably more complicated CoO with rock salt structure. Due to high electron affinity of surface molecules, oxygen element gets attached to the molecules on the surface of the prepared thick films.

3.3. Crystallinity

It describes degree of structural order in a solid. Crystallinity index is denoted by I_{cry} can be calculated through comparison of crystallite size obtained from XRD and that obtained by SEM.

$$I_{\text{cry}} = \frac{D_p}{D}, (3)$$

where, $D_p = 116.70$ nm is the particle size from SEM and $D = 18.20$ nm by using Debye–Sherrer formula.

When I_{cry} is close to 1, it is assumed that the crystallites represent monocrystalline units while larger value of I_{cry} means that the particles are of polycrystalline type.

From XRD and SEM, $I_{\text{cry}} = 6.41$ for cobalt oxide thick film, it's much greater than 1 implies that the prepared thick films show polycrystalline type. Result shows particle has polycrystalline nature and good crystallinity.

3.4. Electrical characterization

The D.C. resistance of cobalt oxide prepared sample was measured by using half bridge method as a function of temperature in home built static gas measurement system. This system consists of glass chamber and heater of nichrome wire having Resistance-120 Ohm at room temperature. The heater was used to change the film sample temperature from room temperature 30 to 350 °C. In half bridge method the value of $R_{\text{ref}} = 10$ M and 30 V$_{DC}$ power supply were used.

3.4.1. Sample resistance. The resistance of the thick film samples was determined using following equation

$$R_{\text{sample}} = R_{\text{ref}} \left\{ \frac{V_{\text{in}}}{V_{\text{out}}} - 1 \right\}. \tag{3}$$

Readings of temperature versus output voltage were taken by changing temperature 10 °C. The D.C. resistance of the films was measured by half bridge method in air atmosphere at 30 – 350 °C. The resistance of cobalt oxide thick films found to be decreases with increase in temperature. This gives the confirmation of semiconducting behaviour of Co₃O₄ material by obeying $R = R_0 \exp(-\Delta E/kT)$ in the 30 – 350 °C temperature range. Fig. 4 shows the change in resistance of pure Co₃O₄ thick films with respect to change in temperature (K).
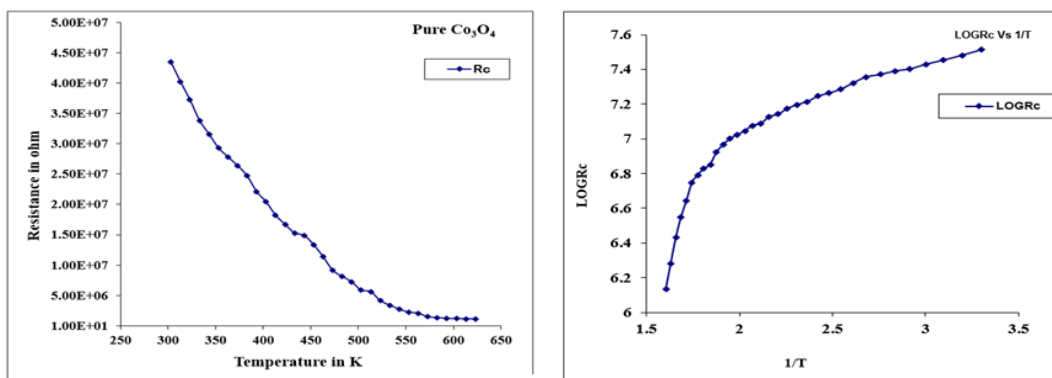

FIG. 4. Plot of resistance against temperature (a) and $\log R$ against inverse temperature (b) for Co₃O₄ thick films

3.4.2. Resistivity of Co$_3$O$_4$ thick films. The resistivity of prepared thick films was calculated as function of temperature within temperature range. The exponential nature of graph shows the resistance decreases steadily to lowest saturation level with respect to increase in temperature. The resistivity of thick films at constant temperature is calculated using equation

$$\rho = \frac{Rbt}{l}, \tag{4}$$

where, ρ is the resistivity of the film, R is the resistance at room temperature, $b = 1.25$ cm is the breadth of film, t – thickness of the film, $l = 2.5$ cm is the length of the film.

To calculate resistivity of unannealed thick film, $R = 4.791 \times 10^7$ Ω, $t = 38$ μm were taken. The value of resistivity ρ is 910.38 Ωm and has maximum with the corresponding conductivity 1.098×10^{-3} Ω^{-1}m^{-1} and has a minimum. The resistivity of pure Co$_3$O$_4$ thick films decreases with increase in annealing temperature. It represents the development of a semiconducting nature in the film. The conductivity is inverse of resistivity and is computed from the relation $\sigma = 1/\rho$, where σ is the conductivity. The electrical resistivity and conductivity values are found out at various annealing temperatures and are mentioned in table. From electrical properties, we observed that the electrical conductivity of pure Co$_3$O$_4$ thick films increases with increase in annealing temperature, films deposited onto nonconductive substrate (250 – 400 °C) as mentioned in Table 4. In fact, annealing treatment provides sufficient thermal energy to the crystal which facilitates the electron delocalization through the elimination of a large number of defects [16].

TABLE 4. Electrical parameters of Co$_3$O$_4$ thick film sensor annealed at different temperatures

Annealing temperature °C	Resistivity Ωm	Electrical conductivity 10^{-3} Ω^{-1}m^{-1}	T.C.R. per kelvin	Activation energy $\times 10^{-4}$ eV	
				At low temp.	At high temp.
250	782.57	1.28	−0.0036	0.78	2.71
300	634.42	1.58	−0.0044	0.35	6.43
350	570.74	1.75	−0.0048	0.32	9.59
400	365.55	2.74	−0.0059	0.29	12.44

3.4.3. Temperature Coefficient of Resistance (TCR) of Co$_3$O$_4$ thick film. The temperature coefficient of resistance (TCR) of pure Co$_3$O$_4$ thick films is calculated by using equation (6). Temperature coefficient of resistance is found negative to pure Co$_3$O$_4$ thick film samples. The negative sign indicates the semiconductor behaviour of the prepared pure Co$_3$O$_4$ thick films. Low resistivity of cobalt oxide thick film samples corresponds to a high TCR value or vice versa. TCR of pure Co$_3$O$_4$ unannealed thick film is found $-0.0115/k$. The observed value of TCR decreases as annealing temperature increased.

To obtain the value of T.C.R. using graph following equation is used

$$\text{TCR}(\alpha) = \frac{1}{R_0}\frac{\Delta R}{\Delta T} = \frac{\text{Slope}}{R_0}, \tag{5}$$

per degree Kelvin.

3.4.4. Activation energy of Co$_3$O$_4$ thick films. The activation energies at the low temperatures and the high temperatures of prepared spinel type Co$_3$O$_4$ thick films were calculated using Arrhenius plot. Fig. 4(b) shows graph of $\log R$ in ohm versus reciprocal of temperature $(1/T)$ in Kelvin for Co$_3$O$_4$ thick films. The Arrhenius plot has two distinct regions of temperature namely low and high temperature region. The annealing temperature of films is an important quantity to decide the transition temperature from low region to high region. The observed values of activation energy for Co$_3$O$_4$ unannealed thick film found to be 1.89×10^{-4} and 5.62×10^{-4} eV at low and at high temperature, respectively. The energy of activation within the low temperature region is low as compared to energy within the high temperature region because material passes from one conduction mechanism to a different. This region are regions of temperature conduction, during this region energy of activation decreases because a tiny low thermal energy quite sufficient for the activation of charge carriers to require part within the conduction process. Hence increase in conductivity within the lower temperature region may be attributed to the increase of charge mobility. It shows more thermal durability with increase in annealing temperature.

The activation energies are calculated by using the Arrhenius relation

$$R = R_0 e^{-\Delta E/k_B T}, \tag{6}$$

where, R_0 is the pre-exponential factor, ΔE is the activation energy, k_B is the Boltzmann constant and T is the absolute temperature.

The activation energy ΔE for Co_3O_4 films is calculated from the slope of the plot the $\log R$ vs $(1/T)$ and is given by $\Delta E = 2.303 k_B \times$ slope of the graph. At low and high temperatures, its values in electron volt are mentioned in table [14].

It shows that the electrical behaviour of the NPs was studied by measuring the dc conductivity as a function of temperature T, this results reveals that the materials are characterized by semiconductor behaviour i.e. by increasing the temperature, more and more charge carriers can overcome the energy barrier and participate in the electrical conduction is assigned to elevated temperatures provide enough energy for charge carriers to hop among sites or even from defects involving singly charged oxygen ions [17]. These oxygen defects would add additional charge carriers to increase conductivity.

4. Conclusion

Cubic structured Co_3O_4 thick films with different thickness have been successfully deposited on glass substrate by the simple, cost-effective screen-printing technique. The structural, morphological and electrical properties have been systematically investigated for Co_3O_4 thick films with annealing temperature. The films were deposited at room temperature (unannealed) and annealed in the temperature range 250 to 400 °C. The XRD analysis reveals that Co_3O_4 thick film shows a polycrystalline nature and cubic structure having a preferential orientation along the (311) plane. The high degree agglomeration of spherical shaped grains was observed. Increase in the thickness of the Co_3O_4 films increased the crystallinity as well as morphological properties. The crystallite size calculated using Debye–Scherrer equation for strongest peak, locating at (311) plane at $2\theta = 36.75$ °, are estimated 18.52 nm. From SEM, observed that Co_3O_4 nano particles are highly agglomerated and are spherical shaped with average particle size is 116.7 nm. Spherical grain size increases with respect to annealing temperature and its maximum 83.5 nm when thick film is unannealed. Surface area decreases from 20.60 to 12.698 m²/gm with increase in annealing temperature from $250 - 400$ °C and is a minimum for unannealed film. The result shows grain size increases and specific surface area decreases as annealing temperature increased. Highly porous film shows high sensitivity. EDAX pattern shows that presence of chemical element as well as purity of Co_3O_4 NPs. The EDAX results obtained for spinel type cobalt oxide thick are in good agreement with reported output. The dislocation density, lattice strain was calculated to obtain information about structural properties. The observed changes takes place due to point defects and crystallite size. The higher peak intensities are due to better crystallinity. From electrical characterization, resistivity decreases from 910.58 to 365.55 Ωm with increase in annealing temperature. It means that cobalt oxide thick films shows semiconductor behavior. The value of electrical conductivity and activation energy at high temperature increases 1.09×10^{-3} to 2.74×10^{-3} $\Omega^{-1}m^{-1}$ and 5.62×10^{-4} to 12.44×10^{-4} eV as annealing temperature increased respectively. A study of these nanoparticles' temperature-dependent dc conductivity illustrated exponential behaviour confirming their semiconductive nature. Also, activation energy is affected by the sensor operating temperature. Additionally, the voids were filled up with the O_2 after annealing which enhanced the probability of main band transitions. From these results, we conclude that the annealing temperature strongly affects the structural, morphological and electrical properties of cobalt oxide thick films. However further investigation and optimization still need to be done for doped cobalt oxide thick films.

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